APPLICATION FOR UNITED STATES PATENT

METHOD OF PRODUCING MOLECULAR PROFILES OF ISOPARAFFINS BY LOW EMITTER CURRENT FIELD IONIZATION MASS SPECTROMETRY (LAW 908)

Applicants: Chang Samuel Hsu and Gary J. Dechert

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BACKGROUND OF THE INVENTION

Field Ionization Mass Spectrometry (FIMS) is well suited to hydrocarbon analysis. For normal paraffins and naphthenes, FIMS may be used to empirically determine the distribution of hydrocarbons as a function of carbon number or molecular weight. Their concentrations can be determined from relative ion abundance or peak intensities in the FIMS spectra. For example, U.S. Patent 5, 644,129 teaches the use of FIMS for just such a purpose. FIMS has also been found useful in the study of high molecular weight hydrocarbons. See for example, Field Ionization Mass Spectrometric Study of High Molecular Weight Hydrocarbons in a Crude Oil and a Solid Bitumen, Jose C. de Rio et al, Organic Geochemistry 30 (1999).

FIMS has not, however, been successfully used for the direct determination of the carbon number or molecular weight distribution of isoparaffins.

Conventional electron - impact ionization and even chemical ionization produce extensive fragmentation of isoparaffins, resulting in the absence of molecular or pseudo-molecular ions in the mass spectra. Conventional field ionization techniques such as those used in U.S. Patent 5,644,129 also result in a high percentage of isoparaffin molecular ions being broken apart to form fragment ions. The carbon number distribution of

isoparaffins is, therefore, currently estimated by comparing their retention times eluting off a non-polar "boiling point" gas chromatographic column with those of normal paraffins. Due to substantial overlap of components and broad distributions of isoparaffins, such estimation techniques are often not accurate.

This invention has discovered a means for producing intact molecular ions for isoparaffins for direct mass measurement.

SUMMARY OF THE INVENTION

The present invention is a method for directly measuring the carbon numbers and molecular weights of isoparaffins using field ionization mass spectroscopy. The emitter current is lowered to below a threshold value that would substantially reduce or eliminate fragmentation of isoparaffin molecular ions.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 shows a diagram of a field ionization mass spectrometer.

Figures 2A&2B show field ionization mass spectra for dotricotane mass spectrometer at a high (30mA) and a low (12mA) emitter current.

Figures 3A&3B show field ionization mass spectra of cholestane at a high (30mA) and a low (12mA) emitter current.

Figures 4A&4B show field ionization mass spectrum of squalane, an isoparaffin, at a high (30 mA) and a low (12mA) emitter current.

Figure 5 traces AB&C show chromatograms of a low boiling point isoparaffin mixture.

Figure 6 shows a field ionization mass spectrum of a low boiling point isoparaffin mixture using the present invention.

Figure 7 shows a field ionization mass spectrum of a high boiling point isoparaffin mixture using the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The practice of the present invention utilizes a conventionally arranged field ionization mass spectrometer adapted to permit varying the emitter current without substantially varying the emitter potential. Referring to Figure 1, there is shown, diagrammatically, a field ionization mass spectrometer. A high electric field is created between the emitter (10) and a counter electrode (12) by imparting a potential of about 8 to 12 kilovolts on the emitter made of a fine wire, and imparting a negative potential of about -1 to -4 kilovolts on the counter electrode. The close proximity of the emitter to the counter electrode, typically of the order of a few millimeters, produces a relatively strong electric field of the order of 10^{10}-10^{12} volts/centimeter. The emitter is typically "activated" in an organic vapor to grow dendrites around the surface of the emitter for increased ionization efficiency. A sample to be analyzed is introduced into the region between emitter and counter electrode by conventional means such as a direct insertion probe, or alternatively, a batch inlet system, or a gas chromatograph. In a preferred embodiment, the insertion probe may be controllably heated from room temperature to about 450°C by conventional means. Ions formed in the field are expelled out of the ion source and accelerated by a voltage on the order of 8-10 kilovolts, whereby a mass analyzer (14), such as a magnetic type mass spectrometer is used in a

conventional manner to analyze ions at high kinetic energies. In operation, the analysis apparatus is maintained under high vacuum, typically below 10^{-5} torr. In addition to the emitter potential, conventional FIMS apparatus apply a heater current "Ie" to the emitter, generally employed to avoid or reduce condensation of sample molecules on the emitter. The FIMS apparatus employed in the practice of the present invention, however, has been adapted to permit varying the emitter current, here shown at (20), without substantially varying the emitter potential.

By reducing the emitter current, substantially intact molecular ions of isoparaffin samples are obtained for direct field ionization mass spectrometric determination of carbon number and molecular weight distributions.

The range of emitter currents useful in the practice of this invention will vary in relation to the surface area and configuration of the emitter. Accordingly, to establish an operating range of emitter currents, a user of this invention may vary the emitter current from relatively high values while obtaining the FI mass spectra for a known isoparaffin sample to establish an operable range of emitter current. This upper limit of the emitter current corresponds to the value that would substantially reduce or eliminate fragmentation of the isoparaffin molecular ion(s). To obtain greater than about 50% of molecular ions for isoparaffins, the emitter current is typically set below 20 mA for a fine wire emitter having a diameter ranging from about 5 to about 50 microns. Lower fragmentation is obtainable by lower emitter currents with decreasing sensitivity. In a preferred embodiment an emitter current range for isoparaffin molecular weight and carbon number determinations ranges from about 3mA to about 20 mA for an emitter ranging from about 5-50 microns in diameter.

The following examples illustrate embodiments of the present invention:

Example 1.

A VG-ZAB high performance mass spectrometer was fitted with a field ionization emitter from Linden ChroMas Spec. The emitter was fashioned from a tungsten wire having a nominal diameter of about five (5) micrometers. The emitter wire was "activated" by the manufacturer to produce dendrites around the wire to increase the area of high electric field. Samples for analysis are introduced via a direct insertion probe that was temperature programmable from room temperature to about 500°C. The foregoing apparatus is housed in a vacuum chamber capable of sustaining a vacuum of about 10^{-6} torr, by conventional means.

Commercial samples of dotricotane ($C_{32}H_{64}$), cholestane ($C_{27}H_{48}$) and squalane ($C_{30}H_{62}$) were chosen to illustrate application of the invention to analysis of normal paraffins, naphthenes, and isoparaffins, respectively. Mass spectra were obtained for the dotricotane and cholestane samples, first using conventional emission currents of about thirty (30) mA, followed by analysis using a low emitter current of about twelve (12) mA. The FI mass spectra obtained for dotricotane and cholestane at high and low emitter currents are shown in Figures 2A, 2B, 3A, and 3B respectively. As can be seen in the drawings, there is no substantial difference between the high and low emitter current mass spectra for these samples of normal paraffins and naphthenes.

Mass spectra were then obtained for the squalane sample, which is a known highly branched isoparaffin. The mass spectrum shown in Figure 4A is that obtained for the squalane sample using conventional emitter current levels, i.e., 30 mA for this emitter configuration. No molecular ion is obtained. The

mass spectrum was then obtained using the low emitter current of the present invention. The mass spectrum of Figures 4B shows that molecular fragmentation has been substantially reduced or eliminated, leaving essentially the molecular ion at 422 daltons.

Example 2

Comparative analytical techniques were used to analyze two additional commercial isoparaffins containing products. The first Sample A was a low boiling point product, having an initial boiling point of 320°F and a dry point of 349°F. The second Sample, B, was a high boiling point product, having an initial boiling point of 523°F and a dry point of 594° F.

GC/MS Chromatograms were obtained for Sample A, and are shown in Figure 5. All of the components eluting off a boiling point GC column between nC_9 (approx. 3.0 minutes) and nC_{11}(approx. 8 minutes). Chromatograms 5A (142 Daltons) and 5B (156 Daltons) show a presence of C_{10} and C_{11} isoparaffins, chromatogram 5C shows substantially no presence of C_{12} isoparaffins (i.e. zero response in the mass 170 chromatogram). Overlap between C_{10} and C_{11} isoparaffins and the elution of some C_{11} isoparaffins ahead of nC_{10} illustrate the shortcoming of these analytical techniques for defining carbon number distribution of isoparaffins based on the retention times of normal paraffins.

Sample A was then analyzed using the techniques taught in this invention. The low emitter current mass spectrometer described in Example 1 was used to analyze Sample A. The results, shown in Figure 6, reveal the distribution of the isoparaffins as approximately 53% C_{11} isoparaffins, approximately 42% C_{10} isoparaffins, and about 5% C_{12} isoparaffins. Remaining composition is revealed to be C_{10} to C_{12} 1-ring naphthenes.

Sample B was then analyzed in a similar manner. All components elute between nC_{14} (approx. 14 minutes) and nC_{20} (approx. 25.5 minutes) on a boiling point GC column. However, due to the severe overlap of the components, this conventional technique is unable to determine the isoparaffins.

Sample B was then analyzed using the low emitter current mass spectrometer. The results, shown in Figure 7, reveal that Sample B comprises a mixture of naphthenes (greater than about 95%).

The homologous series of masses 224 (224, 238, 252, 266, 280, 294, 308, and so on) are the molecular ions of 1-ring naphthenes. It also contains lesser amounts of 2-ring naphthenes; with isoparaffins constitute minor components in the product. The intense m/z 57 peak indicates the highly branched nature of the alkyl side chains of these naphthenes.